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Fluorescence properties of submonolayers of rhodamine 6G in front of a mirror

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Fluorescence properties of submonolayers of rhodamine 6G have been measured as a function of distance to an aluminum mirror. For distances less than 5 nm (spacer layers of 1 nm thickness were used) a broadening of the emission spectrum is observed. The fluorescence lifetime has been measured for distances up to 6 nm. The broadening of the fluorescence spectra and the shortening of the lifetime observed when the sample is close to the mirror are attributed to efficient energy transfer from the monolayer to the mirror. The experiments clearly demonstrate that both volume and surface contributions must be considered in this energy-transfer process.

INTRODUCTION

The radiative dynamics of molecules that luminesce in front of a mirror have been studied extensively during the past decades.[1–3] The metal surface influences the radiative as well as the nonradiative properties of the emitting molecules. The influence of the mirror on these dynamics shows a marked distance dependence. In case of emitter–mirror distances on the order of the emitted wavelength, an oscillatory behavior of the fluorescence lifetime with distance has been found.[2] This effect is ascribed to the interference between directly emitted waves and waves reflected from the mirror. For distances less than about 10 nm the lifetime of the excited state is dominated by radiationless energy transfer to the metal substrate. The excited molecule interacts through the near field with the electron gas of the metal and the excitation energy is dissipated through various scattering processes into the bulk. A reduction of the excited state lifetime by several orders of magnitude is observed. In the case of flat silver surfaces the emission is even completely quenched.[4]

Absorption of energy by the electrons in the metal requires momentum conservation. Three different sources can supply this momentum:[5–7] (1) in the bulk—scattering by phonons, impurities, and the crystal potential; (2) scattering by the metal surface; and (3) from the spatial variation of the near-field of the excited molecule itself. Process (1) dominates at larger distances ($\gtrsim 5$ nm), for which an inverse cube distance dependence was calculated. A d^{-4} dependence has been derived for processes (2) and (3). These processes are expected to dominate for small molecule–metal distances ($\lesssim 5$ nm).

A considerable amount of work has been devoted to line shape studies of physisorbed molecules.[5,8] Two different techniques have been applied. By means of infrared reflection–absorption spectroscopy information is obtained about the vibrational frequencies and bandwidths. These quantities can be studied as a function of surface coverage.[8,9] The observations are explained in terms of lateral dipole–dipole and dipole–image-dipole interactions.[10] Electron energy-loss spectroscopy has been employed to study electronic as well as infrared transitions of adsorbates on metal surfaces.[5,11] In all cases a broadening of the spectral features is observed with respect to multilayer values. This is usually attributed to a reduced excited state lifetime[5,8,11] caused by interaction between the physisorbed molecules and the metal.

For distances shorter than 1 nm chemical effects will also alter the line shape and line position.[3,5] Chemical bonding to the substrate also affects the vibrational frequencies. Another effect that may occur is electron transfer from the adsorbate to the substrate.[3,5]

In this paper we report on a study of the fluorescence spectra of submonolayers of rhodamine 6G (R6G) spaced by amylose–acetate ester layers from a plane aluminum mirror. Aluminum instead of silver was chosen as a substrate because the luminescence is less efficiently quenched in this case. The distance between the mirror and the R6G molecules was varied over a range of 1–6 nm by use of transparent polymer layers of 1 nm thickness. The advantage of using polymer spacer layers instead of conventional fatty acid monolayers, is that a higher spatial resolution can be achieved (1 nm vs 5 nm, respectively). This is caused by the fact that only one polymer spacer layer is transferred per dipping cycle. In this way the formation of bilayers is prevented.[2,12]

We found that the linewidth of the emission spectrum depends on the distance of the sample to the mirror. In addition, we observed for small distances a line broadening. We also measured the fluorescence lifetime and the apparent quantum yield of emission as a function of emitter–mirror distance. All observations can be explained assuming energy transfer from the monolayer to the mirror occurs, using existing theory.

To the best of our knowledge this is the first time that it is shown that the spectral width of a monolayer depends on the distance to a mirror.

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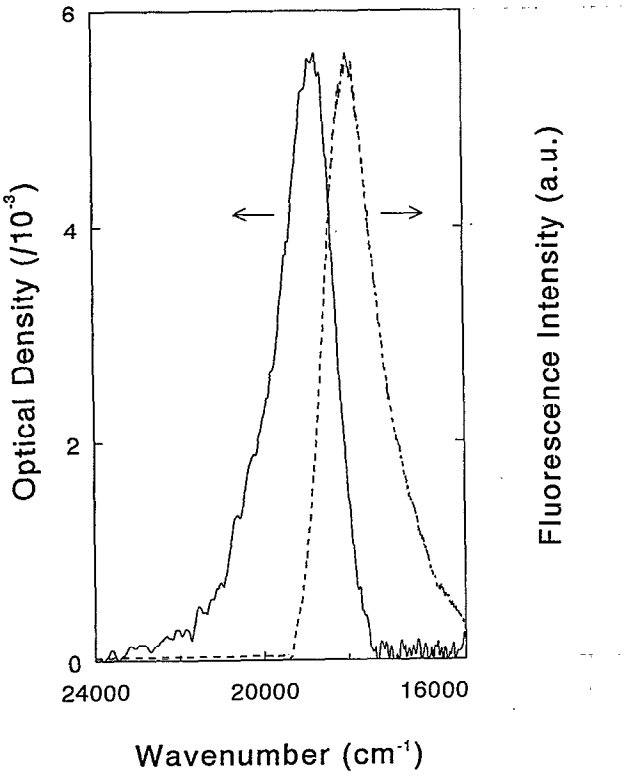

FIG. 1. Absorption (solid curve) and fluorescence (dashed curve) spectra of submonolayers of rhodamine 6G on a Corning 7059 glass substrate. The excitation wavelength was 488 nm.

EXPERIMENT

R6G was obtained from Lambda Physik, and was used without further purification. R6G monolayers were prepared by the dipping technique. The dipping proceeded at a rate of 0.25 mm/s from $5\times10^{-5}M$ ethanolic solutions. As is evident from the absorption spectrum (Fig. 1), no sign of aggregation is observed.[13]

The substrates were prepared by evaporation, at a pressure of 10^{-5} Torr, of thick aluminum layers onto Corning 7059 microscope slides. The slides were cleaned before use in chromic acid, and were rinsed ultrasonically with milli-Q water, acetone, chloroform, and hexane.

The spacer layer consisted of amylose–acetate ester, and was made by the Langmuir–Blodgett technique at a surface pressure of 7 mN/m.[12] The subphase was highly purified water (milli-Q), at a temperature of 22 °C. A monolayer was transferred during every upstroke.

The fluorescence spectra, observed in the direction perpendicular to the substrate surface, were recorded using an intensified optical multichannel analyzer (Princeton Instruments). The 488 nm line of an argon-ion laser (Spectra Physics) was used as excitation source.

The fluorescence lifetime of R6G monolayers were measured using a time correlated single photon-counting system. A cavity-dumped mode-locked argon-ion laser (Coherent, Inc.) operating at a repetition rate of 94 kHz (514.5 nm) was used as an excitation source. The photomultiplier used was a Hamamatsu microchannel plate (R1564U-01). While the intrinsic time resolution of the detection system is 33 ps for ultrafast excitation, the actual time resolution in our experiment was 45 ps, due to the use of a mode-locked Ar^+ laser as an excitation source.

THEORETICAL CONSIDERATIONS

For a calculation of the influence of aluminum substrates on the fluorescence lifetime of physisorbed R6G, we employ a theory developed by Persson and co-workers.[5–7] In this theory the excited state lifetime for an oscillating dipole at a small distance d from the metal surface ($kd\ll1$) is

$$T_{1,\mathrm{NR}}^{-1}(d)\approx T_{1,\infty}^{-1}\left\{1+\frac{\eta}{8}(dk)^{-3}\left[2\,\mathrm{Im}\left(\frac{\epsilon_m(\omega)-\epsilon_1}{\epsilon_m(\omega)+\epsilon_1}\right)+6\xi\frac{1}{k_F d}\frac{\omega}{\omega_p}+18\frac{\omega_F}{\omega_p}\frac{\omega}{\omega_p}\frac{1}{k_F d}\right]\right\}, \quad (1)$$

where $T_{1,\infty}$ is the fluorescence lifetime at an infinite distance from the mirror, k is the magnitude of the wave vector at the emitted frequency ω, $\epsilon_m(\omega)$ is the (complex) metal dielectric constant, ϵ_1 is the dielectric constant of the medium in which the dipole is embedded, and η is an orientational parameter ($\eta=3/2$ for a perpendicular dipole and $\eta=3/4$ for a parallel dipole). The last two terms between square brackets contain electron–gas parameters of a typical metal. Here k_F is the Fermi wave vector, ω_F the Fermi frequency, ω_p the plasma frequency, and $\xi\approx1$ (Ref. 7) is a constant which depends on the electron–gas density. The last term between square brackets is valid for the case where $k_F d\gg\omega_F/\omega$. For a derivation of Eq. (1) and a detailed discussion of the different terms in Eq. (1) we refer to the work of Persson and co-workers.[5–7]

The three terms between square brackets signify the different sources of momentum, as mentioned in the Introduction. The first term represents the bulk contribution to the damping rate, and is identical to the classical result where the interaction of the transition dipole with the electromagnetic field of its image dipole is considered.[1] In this theory the out-of-phase (imaginary) part of the reflected field determines the nonradiative lifetime $T_{1,\mathrm{NR}}$, while the in-phase (real) part affects the frequency shift $\Delta\omega$. In deriving this term a steplike metal surface was assumed. Furthermore, a bulk metal dielectric constant is used, while surface contributions to the energy decay are neglected. In Eq. (1), however, surface contributions are accounted for by the second term between square brackets, where the required momentum is supplied by the surface potential. In the last term momentum originates from the spatial variation of the near field of the dipole. The distance behavior of the three terms between square brackets is different. For the volume scattering a d^{-3} behavior was calculated, while a d^{-4} behavior was obtained for the other two contributions. Volume contributions are expected to dominate for metal substrates in the frequency region of strong interband transitions. This expectation is indeed borne out for molecule–surface separations down to 1 nm.[3,14] For nearly free-electron-like metals the d^{-4} terms are dominant at

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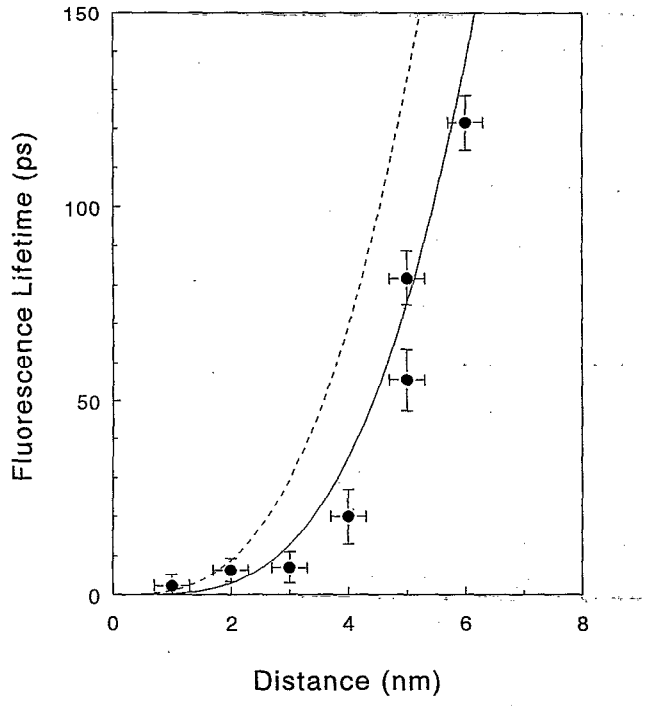

FIG. 2. Fluorescence lifetime as a function of emitter–metal distance (solid dots). The solid line results from the calculation according to Eq. (1); the dashed curve is obtained when only bulk contributions to the energy-transfer rate are incorporated.

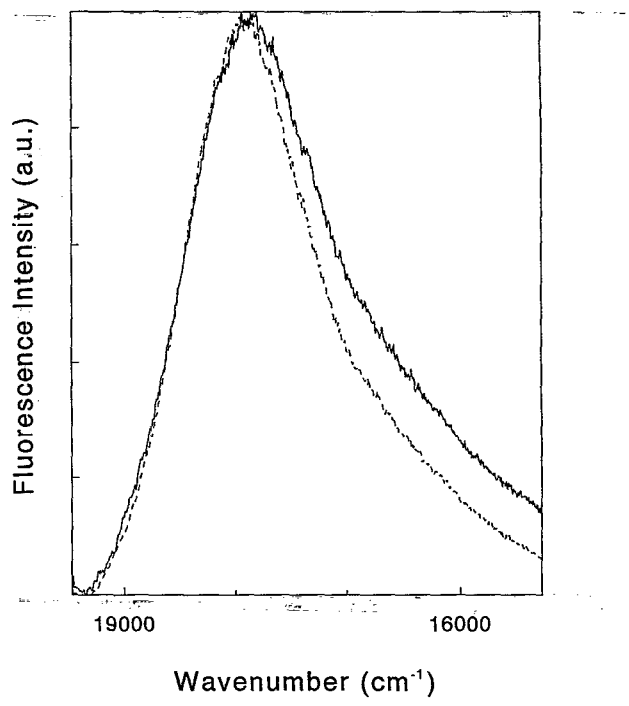

FIG. 3. Fluorescence spectra of rhodamine 6G submonolayers separated by a distance d from the aluminum surface by one ($d=2$ nm, solid line), and five spacer layers ($d=6$ nm, dashed line). The excitation wavelength was 488 nm.

small molecule–surface separations ($d\leqslant 5$ nm), and a fluorescence lifetime is calculated which is about 10 times shorter than would be estimated, if only bulk scattering processes were taken into account.

RESULTS AND DISCUSSION

The results of fluorescence decay measurements of R6G physisorbed to aluminum substrates are given in Fig. 2, where the fluorescence lifetime is plotted vs the distance between the emitters and the mirror. Fluorescence decay curves could be fitted to a single exponential, in agreement with the work of Leitner *et al.*[15] For molecule–surface distances shorter than ≈ 4 nm the fluorescence decay time was found to be beyond the system response (45 ps). For these distances the fluorescence lifetime was indirectly determined from relative quantum yield measurements. The solid line in Fig. 2 is based on Eq. (1) using a metal dielectric constant $\epsilon_m=-39.2+i11.77$,[16] $\epsilon_1=1.3$, and $T_{1,\infty}=3$ ns, and $\eta=3/4$ corresponding to the known parallel orientation of the R6G molecules with respect to the substrate surface.[17] Furthermore, we used $\omega=3.3\times10^{15}$ rad/s, $\omega_p=2.39\times10^{16}$ rad/s, $\omega_F=1.7774\times10^{16}$ rad/s, and $k_F=1.75\times10^{10}$ m^{-1}.[18] The requirement $k_F d\gg\omega_F/\omega$ is met for the whole regime of emitter–metal distances studied, justifying the expression for the last term in Eq. (1) [for the smallest distance of 1 nm $(k_F d)/(\omega_F/\omega)\approx 3.2$]. The dashed line in Fig. 2 is the classical result,[1] where surface contributions to the damping rate are neglected. Note that incorporation of these contributions in the calculations leads to a substantial better agreement with the experimental data.

In estimating the distance of the emitting layer from the metal surface we presume a native oxide layer of 1 nm thickness to be present at the metal surface.[19] This oxide layer is formed within 2 h of exposure to air, after which it slowly grows until it reaches, after about one month, its final value of about 4 nm. This oxidation process is unavoidable due to the application of spacer layers by the Langmuir–Blodgett technique. All measurements were done within 1 h after preparation.

In addition to lifetime and quantum yield measurements we also measured the distance dependence of the fluorescence spectra for physiosorbed R6G monolayers. In Fig. 3 emission spectra are shown for R6G monolayers separated by one ($d\simeq 2$ nm), respectively five ($d\simeq 6$ nm), polymer spacer layers. A broadening of the spectrum close to the mirror is observed. This broadening appears to be asymmetric due to redshift (70 cm^{-1}) that accompanies this change of line breadth. An estimate of the spectral redshift can be made by using the classical expression for the interaction between an oscillating dipole with its fictitious mirror image.[1] For $kd\ll 1$ this yields the following equation:

$$\Delta\omega=\omega(d)-\omega(\infty)$$

$$=-\frac{q\sigma}{8}(dk)^{-3}T_{1,\infty}^{-1}\,\mathrm{Re}\left(\frac{\epsilon_m(\omega)-\epsilon_1}{\epsilon_m(\omega)+\epsilon_1}\right), \qquad (2)$$

where q is the quantum yield of emission at infinite distance from the mirror. With Eq. (2) we calculate a redshift

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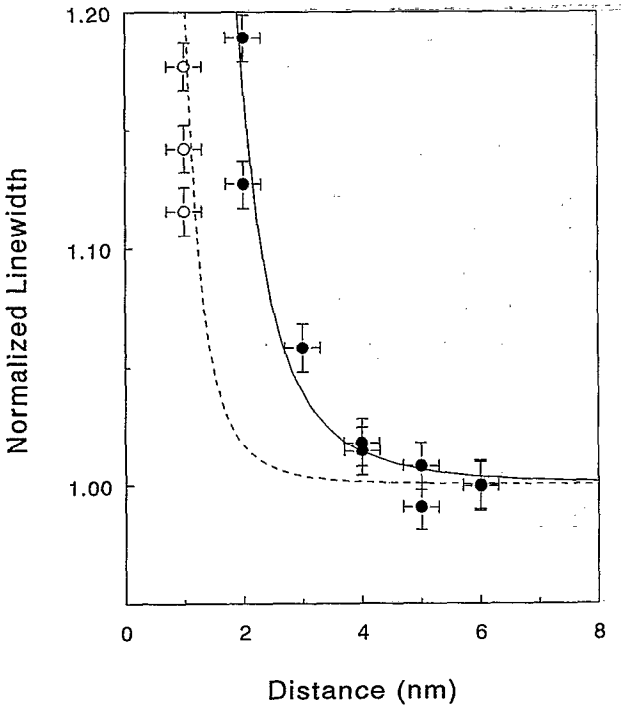

FIG. 4. Plot of the FWHM of the emission spectrum normalized with respect to the FWHM at infinite distance from the mirror, as a function of emitter–mirror distance (solid dots). Also shown are the results of measurements for R6G physisorbed directly onto aluminum (open circles). The solid and dashed lines are based on calculations using Eqs. (1) and (3), whereby $T_2^* = 1$ ps (solid line), and $T_2^* = 100$ fs (dashed line).

of 17 cm^{-1} ($d=2$ nm), which is substantial smaller than the observed redshift of about 70 cm^{-1} (see Fig. 3). It is clear that while the right order of magnitude for the shift is calculated quantitative agreement is not achieved. At this point it is not clear what the source of the discrepancy is.

An estimate of the line broadening can be made using Eq. (1). The effect of the reduced excited state lifetime on the homogeneous damping rate Γ_{hom} can be calculated from[20]

$$\Gamma_{hom}=(2T_1)^{-1}+(T_2^*)^{-1}, \tag{3}$$

where T_1 is the excited state lifetime (longitudinal relaxation time), and T_2^* the pure dephasing time (transversal relaxation time).[20] An effect of the reduced excited state lifetime on the homogeneous linewidth can be expected if T_1 becomes comparable to T_2^*.

The distance dependence of the full width at half maximum (FWHM) of the fluorescence spectra, normalized with respect to the FWHM at infinite distance from the mirror, is plotted in Fig. 4. The width decreases sharply with *increasing* distance and remains constant for emitter–mirror distances larger than 5 nm (solid circles). Also shown are measurements of the FWHM for R6G physisorbed directly onto aluminum surfaces (open circles). The distance dependence of the normalized FWHM is calculated according to Eq. (3) using the expression of Eq. (1) for T_1, where we assume the pure dephasing rate and the inhomogeneous broadening to be independent of emitter–metal distance. The solid line in Fig. 4 is the result of the above calculations where T_2^* was set to 1 ps. For directly adsorbed R6G, agreement with theory is obtained if a pure dephasing time constant of 100 fs is used (dashed line in Fig. 4). In these calculations the thickness of the oxide layer is again assumed to be 1 nm.

The notable difference in pure dephasing times found for R6G directly adsorbed to aluminum and for R6G physisorbed to polymer spacer layers must be attributed to a difference in chemical environment. Fluctuations in the electric field of the conduction electrons, which are felt directly by physisorbed dye molecules, will have a reduced effect on molecules deposited on a spacer layer.

The estimated pure dephasing time of 1 ps for the polymer-spaced dye monolayers is an order of magnitude longer than the value found for molecules dissolved in bulk polymers.[21] However, it is still an order of magnitude shorter than the dephasing times measured for molecules in the gas phase.[20] As stated, the two-dimensional nature of the interaction in our samples is probably the main cause for the long dephasing time found. It would be of interest to confirm the occurrence of such a long dephasing time by another optical technique.

Finally, it should be noted that the excited state lifetime of 250 fs calculated for a distance of 1 nm from the aluminum surface is of the same order as the lifetime estimated for the $^1B_{2u}$ state of pyrazine directly adsorbed to the Ag(111) surface.[11]

Summarizing, we have studied the radiative dynamics of submonolayers of R6G as a function of distance to an aluminum mirror. A shortening of the fluorescence lifetime and a reduction of the quantum yield of emission by several orders of magnitude ($\approx 10^4$) was measured. Also a noticable broadening and redshift of the emission spectra close to the mirror was observed. The dependence of these quantities on the distance between the sample and substrate was measured in steps of 1 nm, enabling a detailed test of existing theory. From the distance dependence of the broadening of the spectra we derived a pure dephasing time of 100 fs for R6G molecules directly absorbed to aluminum, and a pure dephasing time of 1 ps for R6G monolayers deposited on a polymer layer. Most observations are in good agreement with theoretical predictions, if the bulk and the surface contributions to the scattering of electrons in the metal are incorporated.

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